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| 3. ABSTRACT (Maximum 200 words)<br><br>The chemisorption mechanisms of Cl <sub>2</sub> , Br <sub>2</sub> , and I <sub>2</sub> on Si(100) 2x1 are very similar while those of F <sub>2</sub> and O <sub>2</sub> are very distinct. For the heavy diatomic halogens (Cl <sub>2</sub> , Br <sub>2</sub> , and I <sub>2</sub> ), the sticking probability increases with incident translation energies above 0.1 eV, and the largest initial sticking probabilities are obtained at the highest incident energies, with S <sub>0</sub> equal to 95-100% for I <sub>2</sub> and Br <sub>2</sub> , and 80-85% for Cl <sub>2</sub> . At low incident energies the initial sticking probability, S <sub>0</sub> decreases with increasing surface temperature while at high incident energies the sticking probability is independent of surface temperature. In addition, for Cl <sub>2</sub> very low energy molecular beams can be prepared, and the sticking probability is observed to decrease with increasing incident energies between 0.02 eV and 0.06 eV. Therefore, all three heavy diatomic halogens can adsorb via precursor - mediated chemisorption at low incident translational energy and via direct - activated chemisorption activated chemisorption at high incident translational energy 1,2. |  |  |  |   |  |
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(a)  $F_2$ ,  $O_2$  Chemisorption on Si(110) 2x1

The chemisorption mechanisms of  $Cl_2$ ,  $Br_2$ , and  $I_2$  on Si(100) 2x1 are very similar while those of  $F_2$  and  $O_2$  are very distinct. For the heavy diatomic halogens ( $Cl_2$ ,  $Br_2$ , and  $I_2$ ), the sticking probability increases with incident translation energies above 0.1 eV, and the largest initial sticking probabilities are obtained at the highest incident energies, with  $S_0$  equal to 95 - 100% for  $I_2$  and  $Br_2$ , and 80 - 85% for  $Cl_2$ . At low incident energies the initial sticking probability,  $S_0$ , decreases with increasing surface temperature while at high incident energies the sticking probability is independent of surface temperature. In addition, for  $Cl_2$  very low energy molecular beams can be prepared, and the sticking probability is observed to decrease with increasing incident energies between 0.02 eV and 0.06 eV. Therefore, all three heavy diatomic halogens can adsorb via precursor - mediated chemisorption at low incident translational energy and via direct - activated chemisorption at high incident translational energy<sup>1,2</sup>.

We just finished our studies of the chemisorption mechanism for  $F_2$  and  $O_2$  on both Si(100) 2x1 and Si(111) 7x7. Both  $F_2$  and  $O_2$  have chemisorption probabilities that increase with incident translational energy indicating that they have the usual activated chemisorption mechanism at high translational energy. In addition, both exhibit the inverse temperature effect: at high translational energy, the sticking probability increases with increasing surface temperature. This has been seen before for  $O_2$ /Si(100) by Engel and was ascribed to thermally assisted activated chemisorption; however, our results on  $F_2$ /Si(100) & Si(111) show the mechanism is more intricate. For  $F_2$  and  $O_2$  sticking on silicon, the activation barrier is sufficiently small that we can increase the translational energy so high that the sticking probability at 300 K goes to 100% and thus the inverse temperature effect disappears. Therefore, at high translational energy the molecules can directly dissociate without passing through the thermally assisted molecular chemisorption channel or there is more than one activated molecular chemisorption channel. At low translational energy, the  $F_2$  sticking is large and nearly independent of translation energy; this low energy chemisorption was investigated further using STM and is a result of abstraction: when  $F_2$  collides with a clean silicon surface, one atom chemisorbs while the other is ejected into the gas phase<sup>3</sup>. We have also recorded the temperature programmed desorption (TPD) spectra of  $SiF_2$  and  $SiF_4$  from  $F_2$ /Si(100) and  $F_2$ /Si(111) and observed that the maximum coverages and  $SiF_4$  TPD peaks increase with increasing incident  $F_2$  translational energy. This indicates that the barrier to forming  $SiF_3$  and  $SiF_4$  species is greater than the barrier to forming  $SiF$  adsorbates and explains why only atomic F and  $XeF_2$  are able to spontaneously etch silicon at 300 K. Therefore, although F and  $XeF_2$  are preferable etchants for continuous etching of silicon because they form multilayer  $SiF_x$  adsorbates, for digital etching thermal  $F_2$  is the preferred etchant since its absorption is limited to only a monolayer of  $SiF$  and  $SiF_2$ <sup>4</sup>.

(b) STM of Local Adsorbate Structure as a Function of Chemisorption Mechanism

As far as we know, we are the only group to have studied the effect of translational energy upon local adsorbate structure using STM. We have developed a unique machine to dose a crystal surface in ultra-high vacuum with a mono-energetic molecular beam and then examine the adsorbate structure with STM. Using this technique, we have identified the role of the chemisorption mechanism in the formation of adsorbate structures for  $F_2$ ,  $Cl_2$ ,  $Br_2$  and  $O_2$  upon Si(111)-7x7 surfaces at 300 K. We are neither the first group to use STM to study the adsorption of halogens on semiconductors nor the first group to use STM to study etching of semiconductors by halogens, but we are the first group to use STM to study chemisorption as a function of adsorbate incident energy and thus chemisorption mechanism.

When Si(111)-7x7 is dosed with 0.05 eV  $Cl_2$  (precursor-mediated chemisorption), the dominant adsorbate structure is  $SiCl$  islands. The  $SiCl$  islands are hundreds of Angstroms apart at low coverage and nucleate at missing adatom defects. Conversely, for 0.44 eV  $Cl_2$  dosing (direct-activated chemisorption), island formation is not observed and only single site center-adatom preferred chemisorption is present. It is proposed that island formation results from  $Cl_2$  adsorption via a mobile molecular physisorption state that dissociates at the edges of  $SiCl$  islands while the center-adatom preferred reaction results from instantaneous direct-activated chemisorption<sup>5,6</sup>. When the  $Cl$ -Si(111)

7x7 surface is heated to 600 °C and partial desorption occurs, the adsorbates structure is independent of adsorption mechanisms because the SiCl forms a 2-D lattice gas prior to 2nd-order recombinative desorption as SiCl<sub>2</sub><sup>7</sup>.

For F<sub>2</sub> chemisorption on Si(111) 7x7, there is no intrinsic physisorption state, and therefore no island formation is observed at low incident translational energy. Instead, at low translational energy, we observe that the dominant adsorption sites are single reacted adatoms, while at high translational energy, pairs of adjacent reacted adatoms are commonly observed. At low translational energy, the F<sub>2</sub> adsorbs via abstraction whereby when a F<sub>2</sub> collides with the surface, one F atom chemisorbs while the other is ejected into the gas phase. The abstraction mechanism was first identified theoretically by Carter et al<sup>8</sup> and experimentally by Li et al<sup>9</sup>. Our STM results show that this abstraction mechanism accounts for nearly all the chemisorption at low energy because nearly all the adsorption sites are single reacted adatoms. At high translational energy F<sub>2</sub> adsorbs primarily by dissociative chemisorption, and thus we observe adjacent pairs of reacted adatoms. The dominant type of reacted silicon pair is center adatoms from adjacent unit cells; this is most easily seen in the high translational energy Cl<sub>2</sub>/Si(111) 7x7 or Br<sub>2</sub>/Si(111) 7x7 where dissociative chemisorption is almost the exclusive adsorption mechanism. The preference for center adatoms from adjacent units cells is due to the center adatoms being more reactive as well as center atoms from adjacent unit cells being the most closely spaced adatom pairs on the surface along with center-center adatom pairs<sup>10</sup>. The preference for most closely spaced pairs in dissociative chemisorption can be understood from the theoretical work of Carter<sup>11</sup>: chemisorption of F<sub>2</sub> is a two-step process in which, upon collision with the surface, the F<sub>2</sub> forms a transient Si-F<sub>2</sub> species. At high translational energy, the initial momentum of the terminal F atom is so large that it is propelled onto the surface and forms a chemisorption bond at a nearby 1/2 filled dangling bond site. We have done a similar translational energy-STM study on O<sub>2</sub>/Si(111) 7x7<sup>12</sup>.

### (c) Practical Digital Etching

Our digital etching chamber has been constructed and delivered. When will have it assembled and operational by the end of 1994. We will first investigate digital etching of GaAs(100) and Si(100) using Cl<sub>2</sub> and laser induced desorption even though better etch spatial anisotropies can be achieved with electron and ion induced desorption. We have initiated two collaborations to do digital etching with electron and ion induced desorption since these will be of greater interest to industry. We hope our collaborators will provide us with the funding for a plasma source as well as one additional person to perform the experiments. We have set up a collaboration with Intel for work upon digital etching of silicon (Dr. John Carruthers, Intel, Santa Clara). Intel has offered to provide us with substrates and metrology. We hope to expand this collaboration and have applied to Intel for funding for development of practical digital etching. We hope to set up a collaboration with Veeco Instruments (Jim Weldon, Veeco Instruments Inc, Milpitas, CA) for converting a commercial RF ion source into a pulsed ion and electron source for digital etching. We have a collaboration set up with Thermionics Inc (Michael Ricks, Thermionics Inc, Hayward, CA) to develop digital etching chambers for research scale investigations. We have already produced one chamber and after it has been tested, the product will appear in the next Thermionics Catalogue.

- 1 D. J. D. Sullivan; H. C. Flaum, and A. C. Kummel, *J. Phys. Chem.* **97**, 12051 (1993).
- 2 H. C. Flaum<sup>‡</sup>; D. J. D. Sullivan, and A. C. Kummel, *J. Phys. Chem.* **98**, 1719 (1994).
- 3 E. Behringer; H. C. Flaum; J. D. J. Sullivan; D. P. Masson; E. Lanzendorf, and A. C. Kummel, *In preparation for J. Phys. Chem.* (1994).
- 4 E. Behringer; H. C. Flaum, and A. C. Kummel, *Submitted to J. Phys. Chem.* (1994).
- 5 C. Yan; J. A. Jensen, and A. C. Kummel, *Phys. Rev. Lett.* **72**, 4017 (1994).
- 6 C. Yan; J. A. Jensen, and A. C. Kummel, *Submitted to J. Chem. Phys.* (1994).
- 7 C. Yan; J. A. Jensen, and A. C. Kummel, *submitted to J. Phys. Chem.* (1994).
- 8 L. E. Carter; S. Khodabandeh; P. C. Weakliem, and E. A. Carter, *J. Chem. Phys.* **100**, 2277 (1994).
- 9 Y. L. Li; D. P. Pullman; J. J. Yang; A. A. Tsekouras; D. B. Gosalvez; K. B. Laughlin; M. T. Schulberg; D. J. Gladstone; M. McGonigal, and S. T. Ceyer, *personal communication* (1994).
- 10 J. A. Jensen; C. Yan, and A. C. Kummel, *Submitted to Science* (1994).
- 11 L. E. Carter; S. Khodabandeh; P. C. Weakliem, and E. A. Carter, *J. Chem. Phys.* **100**, 2277 (1994).
- 12 C. Yan; J. A. Jensen, and A. C. Kummel, *in preparation for J. Phys. Chem.* (1994).